



Characterization and recycling of cadmium from waste nickel–cadmium batteries

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ARTICLE INFO

Article history:

Received 20 January 2010

Accepted 18 May 2010

Available online 11 June 2010

ABSTRACT

A severe threat was posed due to improper and inefficient recycling of waste batteries in China. The present work considered the fundamental aspects of the recycling of cadmium from waste nickel–cadmium batteries by means of vacuum metallurgy separation in scale-up. In the first stage of this work, the characterization of waste nickel–cadmium batteries was carried out. Five types of batteries from different brands and models were selected and their components were characterized in relation to their elemental chemical composition and main phase. In the second stage of this work, the parameters affecting the recycling of cadmium by means of vacuum metallurgy separation were investigated and a $L_{16}(4^4)$ orthogonal design was applied to optimize the parameters. With the thermodynamics theory and numerical analysis, it can be seen that the orthogonal design is an effective tool for investigating the parameters affecting the recycling of cadmium. The optimum operating parameters for the recycling of cadmium obtained by orthogonal design and verification test were 1073 K (temperature), 2.5 h (heating time), 2 wt.% (the addition of carbon powder), and 30 mm (the loaded height), respectively, with recycling efficiency approaching 99.98%. The XRD and ICP-AES analyzed results show that the condensed product was characterized as metallic cadmium, and cadmium purity was 99.99% under the optimum condition.

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1. Introduction

Recycling of waste batteries is an important subject not only from the viewpoint of treatment of hazardous waste, but also with respect to the recovery of valuable materials due to the fact that waste batteries contain considerable amount of heavy metals such as mercury, lead, nickel, zinc, and cobalt. In addition, the world-wide consumption of batteries is significant (Bernardes et al., 2003; Chang et al., 2009; Vassura et al., 2009). Some laws and regulations were enacted for the collection of such products and several recycling processes for waste batteries were developed by researchers. (Bernardes et al., 2004; Briffaerts et al., 2009; Kuo et al., 2009; Li et al., 2009; Xia and Li, 2004). Nevertheless, less than 2% of waste batteries were recycled in China (Yang, 2007; Zhang et al., 2008). A severe threat was posed due to improper and inefficient recycling of waste batteries. It is reported that huge quantities of electronic waste (e-waste, including waste batteries, waste printed circuit boards, waste liquid crystal display, etc.) have been produced and made a great impact on the environment in China (Huang et al., 2009a; Leung et al., 2006, 2008; Wang et al., 2009; Wong et al., 2007). Therefore, it is urgent to seek an eco-friendly method for resolving the growing problem of waste batteries.

Nickel–cadmium (Ni–Cd) battery is a kind of rechargeable battery. Waste Ni–Cd battery is classified as a hazardous waste in terms of high Cd content, and it should be recycled prior to other

types of batteries. The existing methods of recycling waste Ni–Cd batteries are pyrometallurgy, hydrometallurgy, and biometallurgy. The cycle for biometallurgy is too long though it is a promising method (Zhao et al., 2008; Zhu et al., 2003). Hydrometallurgy is an attractive solution because of it is low energy requirement (Baba et al., 2009; Nogueira and Margarido, 2004). However, the recovered products through hydrometallurgy are still metallic compound, which need further treatment. The traditional pyrometallurgy is extremely hazardous to the environment as a large part of the metals vapors is released into the atmosphere. Vacuum metallurgy separation is a kind of pyrometallurgy with high efficiency and better environmental properties. The difference in vapor pressures of various metals at certain temperature is the principle of separating pure metals from mixed metallic materials by vacuum metallurgy separation. Vacuum metallurgy separation was applied in this study in order to directly obtain high purity metal rather than middle products.

In our previous studies, an integrated process (including dismantling, crushing, vacuum metallurgy separation, and magnetic separation) for recycling waste Ni–Cd batteries was proposed (Huang et al., 2009b). The process provided a possibility for recycling waste Ni–Cd batteries in a large industrial scale. However, the previously investigated batteries were basically composed of homogeneous batteries. In addition, the energy consumption and technology rationality still need to be further developed. Therefore, the characterization of different types of waste Ni–Cd batteries and the optimization of the vacuum metallurgy for recycling Cd from waste Ni–Cd batteries is far from redundant. In order to extend

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the practical fields of vacuum metallurgy separation to the recycling of waste Ni–Cd batteries, the characterization of different brands and models of waste Ni–Cd batteries and the effect of the vacuum on reduction process were investigated in this study. Furthermore, the parameters affecting the recycling of cadmium from waste Ni–Cd batteries through vacuum metallurgy separation were optimized by using the orthogonal design.

The objective of this research was to enrich the vacuum metallurgy separation theory, and provide a theoretic basis for the optimization of operating parameters in scale-up.

2. Materials and methods

2.1. Characterization of waste Ni–Cd batteries

Waste Ni–Cd batteries used in this work were collected and kindly provided by a battery manufacturer. The characterization of metal composition can give useful information to implement suitable recycling processes. To quantify the different materials present in waste Ni–Cd batteries, five types of batteries from different brands and models were selected. They consisted of 153 AAA type, 153 2/3AA type, 102 AA type, 51 C type, and 51 D type.

Characterization processing included dismantling processing and qualitative elemental chemical analysis, and phase identification. These waste Ni–Cd batteries were dismantled and their different components were separated. After dismantling and separation of components, the classified components were weighed.

The qualitative elemental chemical analysis of the initial electrode materials and the residues after vacuum metallurgy separation were determined by inductively coupled plasma atomic emission spectrometry (ICP–AES, IRIS Advantage 1000, THERMO, US) after appropriately dissolved with a mixture 1:1 (v/v) of 37% HCl and 68% HNO₃. Phase identification of electrode materials and all generated products were characterized and analyzed by X-ray powder diffraction (XRD, D/max-2200/PC, Rigaku Corporation, Japan) with Cu K α radiation, operating at 40 kV and 30 mA, where $\lambda = 0.15418$ nm for the Cu K α line. A scan speed of 2° (2 θ) min^{−1} was utilized.

2.2. Vacuum metallurgy separation processing

The chamber pressure was maintained at a level between 1 and 3.1 Pa during the distillation process. Five types of waste Ni–Cd batteries were used as raw materials in each vacuum test. The vacuum tests were divided in two series (V₁ tests and V₂ tests). A series of tests on vacuum metallurgy separation (V₁ tests) were adopted to derive the optimum parameters, and the temperatures were 923, 973, 1023, and 1073 K, heating times were 1, 1.5, 2, and 2.5 h, the loaded heights were 30, 60, 90, and 120 mm, and the

addition of carbon powder (particle size <100 mesh) were 0.5, 1, 1.5, and 2 wt.% in V₁ tests. The other series of tests on vacuum metallurgy separation (V₂ tests) were the additional tests, which were conducted to validate the experimental analysis.

In view of the fact that large numbers of testing factors and at least 256 (4⁴) tests are required to be evaluated. It is impractical to carry out overall tests including all the factors and levels that need to be considered. Therefore, four operating parameters involved in V₁ tests were investigated by a L₁₆ (4⁴) orthogonal design in an attempt to find the optimum operating parameters in scale-up.

All the data in this study were conducted at least three times and the analysis showed an experimental error was always smaller than 5%.

3. Results and discussion

3.1. Characterization of waste Ni–Cd batteries

3.1.1. Characterization through dismantling processing

2/3AA type, AAA type, AA type, C type, and D type of selected batteries were denominated 1, 2, 3, 4, and 5, respectively. A schematic diagram of some typical waste Ni–Cd batteries used in this work, and the internal structure of a dismantled battery showing the target components are shown in Fig. 1.

Waste batteries were a complex product composed by a large variety of materials. These selected waste Ni–Cd batteries mainly consisted of metal shell, electrolyte, cathode, anode, and separator. In dismantling processing, the components of waste Ni–Cd batteries were separated and classified as: metal shell, cathode, anode, separator, and other materials (including electrolyte, plastic, cardboard, etc.). The materials of the metal shells were Ni-plated steel or carbon steel covered with a plastic label. The electrolyte was a solution of KOH or LiOH, which was impregnated in separator. The positive and negative electrodes were isolated by polyethylene, cardboard, or polypropylenes separators. The electrode materials were released from the support plates by twisting. It was observed that the cathode materials were more easily released from the plates than the anode materials. This result demonstrates that high liberation efficiencies of the electrode materials could be attained in a crushing processing.

The classification and the weight of each part in the representative waste Ni–Cd batteries are shown in Table 1.

The results reveal that the average components of metal shell, cathode, anode, and separator in weight distribution of representative waste Ni–Cd batteries were 25.2, 29.8, 24.4, and 7.2 wt.%, respectively. These results indicate that the electrodes are responsible for more than 45 wt.% for all batteries and it represents around 70 wt.% for battery 4. The metal shells, which are

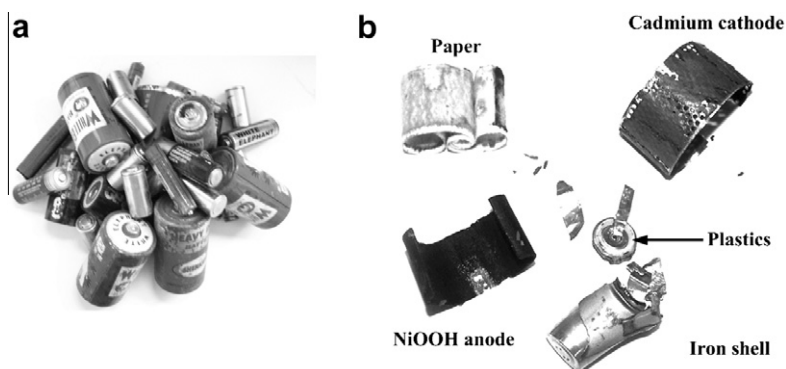


Fig. 1. Schematic diagram of (a) some typical waste Ni–Cd batteries used in this work, (b) the internal structure of a dismantled battery showing the target components.

Table 1

Materials mass balance of the main components of waste Ni–Cd batteries.

Component	Battery 1		Battery 2		Battery 3		Battery 4		Battery 5	
	Mass (g)	Wt.%	Mass (g)	Wt.%	Mass (g)	Wt.%	Mass (g)	Wt.%	Mass (g)	Wt.%
Metal shell	3.47	25.3	2.59	27.3	4.89	24.3	7.10	10.8	26.10	20.1
Separator	1.27	9.3	0.38	4.0	1.13	5.6	4.66	7.1	13.25	10.2
Cathode	2.78	20.3	3.02	31.9	6.60	32.8	23.99	36.5	36.75	28.3
Anode	3.51	25.6	1.99	21.0	5.09	25.3	21.56	32.8	35.71	27.5
Other material	2.25	16.4	1.23	13.0	2.03	10.1	6.97	10.6	16.36	12.6
Loss	0.42	3.1	0.26	2.8	0.37	1.9	1.45	2.2	1.69	1.3
Total	13.70		9.47		20.11		65.73		129.86	

essentially made by carbon steel or Ni-plated steel, correspond to about 25 wt.% of the batteries weight.

3.1.2. Elemental chemical characterization

According to the ICP-AES analyzed results, the metal components found in the representative waste Ni–Cd batteries are presented in Fig. 2. Fe includes the iron contained in the iron shell and supported plate.

The presence of different elements such as Li, Fe, Mn, Zn, and Co was observed and denominated as “other metals”. Other metals mainly consisted of Co, Zn, and Li. The presence of these metals may be attributed to the fact that the plates were not pre-treated. The plates are possibly contaminated by the electrolyte and the paste that covered the plates. The results reveal that the average components of Cd, Ni, Fe, and other metals in the representative waste Ni–Cd batteries were 17.6, 20.4, 31.6, and 2.6 wt.%, respectively. Therefore, the effective recycling of these metals, not only brings benefits in environmental terms, but also brings profit in economical terms.

3.1.3. Phase identification of electrode materials

According to the XRD results, the positive electrodes are made of precipitated hydroxides of nickel (NiOH or Ni(OH)₂). Cadmium hydroxides were identified in all selected batteries. This result is consistent with other literature data (Nogueira and Margarido, 2007). Metallic cadmium was identified in battery 1, 3, and 4. No evidence of CdO was found in all selected batteries.

From the experimental results, it can be seen that it is difficult to obtain the exact Cd contents of the different types of batteries. However, cadmium is the main chemical composition of waste Ni–Cd batteries even the brand and shape are different. By the analysis of these results, it is possible to infer the chemical composition of waste Ni–Cd batteries, which is an important factor in the

definition of a recycling process. Based on the principle of the difference in vapor pressures of various metals at certain temperature, vacuum metallurgy separation was applied in this study due to the fact that Cd can be recycled efficiently through vacuum metallurgy separation even the fluctuation of the Cd content in the waste Ni–Cd batteries.

3.2. Vacuum metallurgy separation processing

3.2.1. In-depth investigation of operating parameters through orthogonal design in vacuum metallurgy separation processing

The recycling efficiencies of Cd at different tests can be calculated as follows:

$$Cd_{\text{recovery}} = \frac{M_i \times \text{wt.\% Cd}_i - M_f \times \text{wt.\% Cd}_f}{M_i \times \text{wt.\% Cd}_i} \quad (1)$$

where, M_i is the loaded initial mass, wt.% Cd_i is the initial Cd concentration (wt.%), M_f is the mass of the material remaining at the crucible after the test, wt.% Cd_f is the final Cd concentration (wt.%) in the crucible.

Orthogonal design is an optimization method by using orthogonal table to scientifically arrange and evaluate the experiment (Taguchi, 1986; Hedayat et al., 1999). The factors influencing the recycling of Cd were investigated under different experimental conditions, and the results related to V₁ tests were shown in Table 2.

3.2.1.1. Effect of temperature on the recycling of Cd. In terms of the results obtained from Table 2, the absolute value and the mean

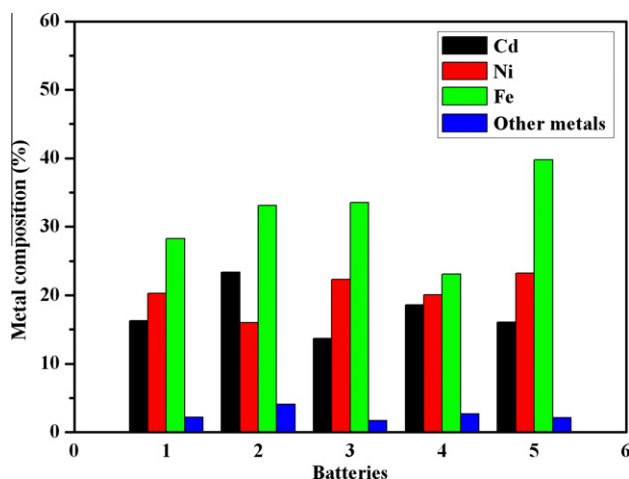


Fig. 2. Metal components of representative waste Ni–Cd batteries.

Table 2Experimental results of the V₁ tests.

Test	Factor				Recycling efficiency (wt.%)
	A ^a	B ^b	C ^c	D ^d	
1	923	1	0.5	30	78.51
2	923	1.5	1	60	82.94
3	923	2	1.5	90	85.03
4	923	2.5	2	120	85.43
5	973	1	1	90	83.59
6	973	1.5	0.5	120	88.54
7	973	2	2	30	90.79
8	973	2.5	1.5	60	92.88
9	1023	1	1.5	120	88.54
10	1023	1.5	2	90	98.52
11	1023	2	0.5	60	96.56
12	1023	2.5	1	30	99.51
13	1073	1	2	60	90.80
14	1073	1.5	1.5	30	98.83
15	1073	2	1	120	99.04
16	1073	2.5	0.5	90	94.78

^a Temperature (K).

^b Heating time (h).

^c The addition of carbon powder (wt.%).

^d The loaded height (mm).

value of four factors were calculated as shown in Table 3. According to the principle of orthogonal design (Taguchi, 1986; Hedayat et al., 1999), the mean value of four factors can indicate the effect of four factors on the recycling of Cd. Therefore, the influencing tendency of four factors on the recycling of Cd can be calculated as shown in Fig. 3. Fig. 3 indicates that the temperature has a significant effect on the recycling of Cd. The recycling efficiencies of Cd increased dramatically with the increase of the temperature and a plateau value was gradually reached. Initially, Cd presented in the form of hydroxide in the Ni–Cd batteries. During the Cd distillation process, the decomposition of Cd monoxides occurred first, and the products of such decomposition were the Cd oxides (Espinosa and Tenorio, 2006a). Carbon powder was added as a reducing agent in this study. Therefore, the system can be analyzed through the following equations (Liang and Che, 1994):

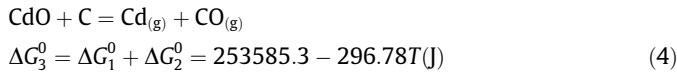


Table 3

The absolute value and the mean value of four factors for the V_1 tests.

Test	Factor				Recycling efficiency (wt.%)
	A ^a	B ^b	C ^c	D ^d	
V ₁	331.91	341.44	358.39	367.64	1454.29
V ₂	355.80	368.83	365.08	363.18	
V ₃	383.13	371.42	365.28	361.92	
V ₄	383.45	372.60	365.54	361.55	
M ₁	82.98	85.36	89.60	91.91	
M ₂	88.95	92.21	91.27	90.80	
M ₃	95.78	92.86	91.32	90.48	
M ₄	95.86	93.15	91.39	90.39	

Note: V indicates the absolute value of four factors; M indicates the mean value of four factors.

^a Temperature (K).

^b Heating Time (h).

^c The addition of carbon powder (wt.%).

^d The loaded height (mm).

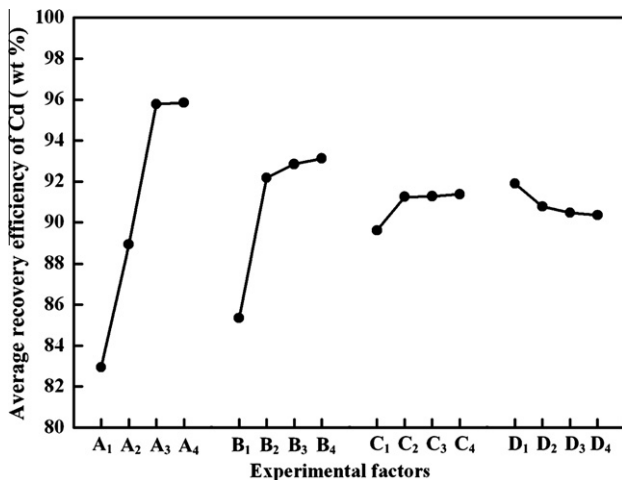


Fig. 3. The influencing tendency of four factors on the recycling of Cd. (A) temperature (K); (B) heating time (h); (C) the addition of carbon powder (wt.%); (D) the loaded height (mm).

Combining with Eqs. (2) and (3), and Cd oxides reduced by carbon powder can be shown in Eq. (4). Cadmium was a metal vapor in the distillation process in the vacuum system. Therefore:

$$\Delta G = \Delta G^0 + RT \ln(p_{\text{Cd}} \cdot p_{\text{CO}}) \quad (5)$$

where, ΔG is the Gibbs free energy at a certain temperature, R is the universal gas constant, T is the temperature (Dai and Yang, 2006).

Since: The gas in the vacuum system was only Cd and CO, therefore,

$$p_{\text{s}}(\text{vacuum}) = p_{\text{Cd}} + p_{\text{CO}} = 2p_{\text{CO}} = 2p_{\text{Cd}}$$

If $p_{\text{s}} = 10^{-m}$ atm,
Then:

$$\Delta G = \Delta G^0 + RT \ln(10^{-2m}/4) \quad (6)$$

As a result, the increase of heating temperature will decrease the Gibbs free energy as shown in Fig. 4a, and the stability of CdO decreased and the CdO can be decomposed easily. In this system, the chamber pressures were maintained at a level between 1 and 3.1 Pa ($m = 4.51\text{--}5$) and the temperatures were high than 923 K during the distillation process. Therefore, the solid Cd can sublime from waste Ni–Cd batteries according to the triple phase equilibrium graph of Cd as shown in Fig. 4b, which was obtained in terms of Eq. (7)

$$\lg P_{\text{Me}}^* = \frac{A}{T} + B \lg T + CT + D \quad (7)$$

where $\lg P_{\text{Me}}^*$ is the vapor pressure of pure metal, T is temperature, A , B , C , and D are constants determined for each metal element (Dai and Yang, 2006).

According to the thermodynamics analysis results, the reduction through carbon powder for CdO is thermodynamically feasible at significantly low temperature in the vacuum system. In addition, recycling of waste Ni–Cd batteries directly to high purity metals can bring large returns in economical terms than to metal oxides. Consequently, vacuum metallurgy separation is of higher efficiency and better economical properties.

Fig. 5a presents the recycling efficiencies of Cd as a function of temperature in V_2 tests. The heating time, the addition of carbon powder, and the loaded height were kept constant as 2.5 h, 2 wt.%, and 30 mm, respectively.

Increasing the temperature increases dramatically the recycling efficiencies of Cd (Espinosa and Tenorio, 2006a; Huang et al., 2009b). It is possible to verify that at 923 K and 973 K, cadmium could not be effectively recycled as shown in Fig. 5a. The recycling of Cd was only partial for the condition studied, and Cd concentration in alumina crucible was still very high in tests conducted at this temperature. Using the same heating time, the addition of carbon powder, and the loaded height, and temperatures of 1023 K, relatively high Cd concentration remained in alumina crucible. On the other hand, in the tests at 1073 K and 1123 K only less than 0.01% of Cd was detected.

3.2.1.2. Effect of heating time on the recycling of Cd. Heating time also has a significant effect on the recycling of Cd. Fig. 3 shows that the recycling efficiencies of Cd increased sharply with the increase of heating time below 1.5 h. This may be attributed to the evaporation of moisture, elimination of volatile materials contained in the sample and the decomposition of hydroxides occurred initially in the heating process. There is no Cd oxide decomposition during this first step. Therefore enough heating time is necessary to the decomposition of all CdO and then evaporation in the vacuum metallurgy separation process. Fig. 3 also indicates that the recycling efficiencies of Cd were almost the same when the heating time exceeded 1.5 h.

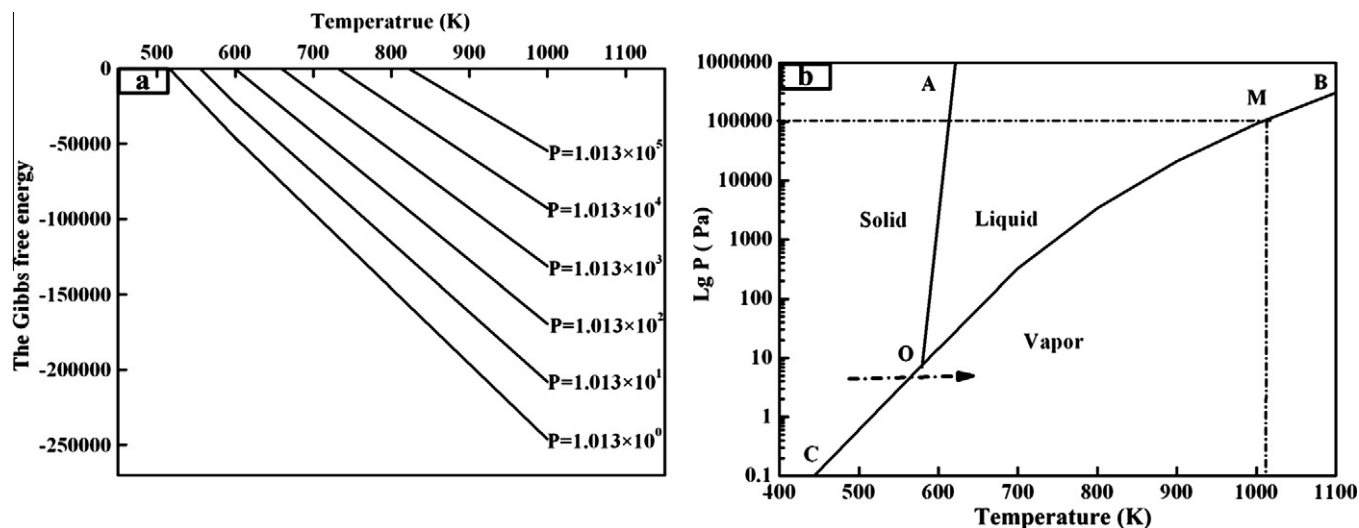


Fig. 4. (a) The relationship of temperature and the Gibbs free energy; (b) the triple phase equilibrium graph of Cd. Point M: the boiling point under the standard atmospheric pressure; point O: the triple phase point, which corresponding temperature and corresponding vapor pressure are 575.9 K and 6.67 Pa, respectively; line OA: liquid–solid equilibrium line; line OB: liquid–gas equilibrium line; line OC: solid–gas equilibrium line.

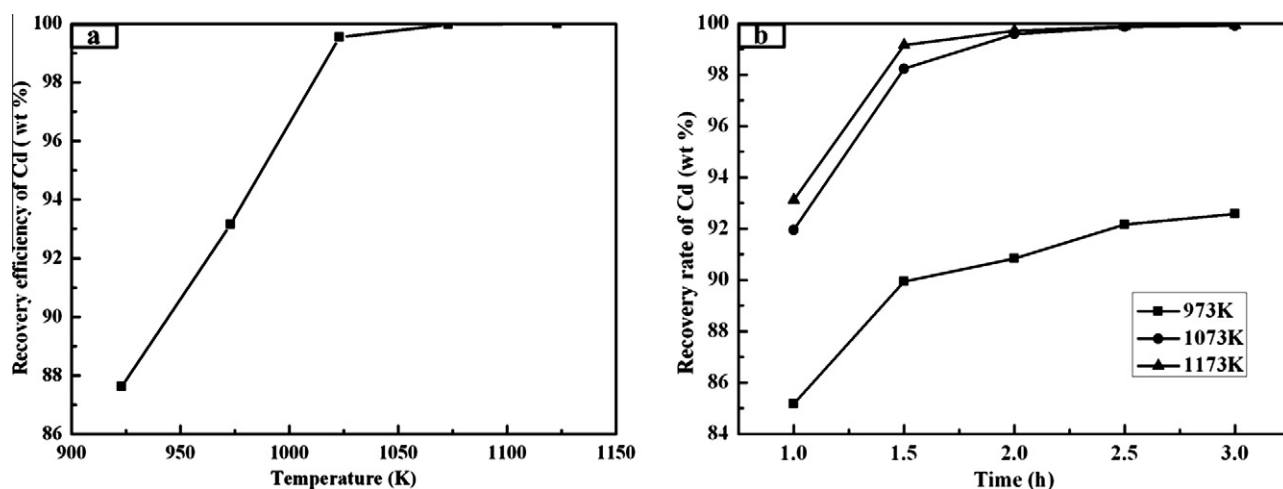


Fig. 5. The recycling efficiencies of Cd in V_2 tests, respectively at 973 K, 1073 K, 1173 K: as a function of (a) temperature; (b) heating time.

Fig. 5b presents the recycling efficiencies of Cd as a function of heating time, respectively at 973, 1073, and 1173 K. The addition of carbon powder was kept constant as 2 wt.%, and the loaded height was kept constant as 30 mm, respectively.

Results obtained by Espinosa and Tenorio (2006b) demonstrated that it was impossible to remove Cd completely from waste Ni–Cd batteries when the temperature was below 923 K or heating time was less than 1 h. Therefore, a higher temperature is necessary to strengthen the vapor pressure for further distillation. Fig. 5b indicates that the recycling efficiencies of Cd increased with the increase of the temperature and heating time. Significant recycling efficiencies of Cd on the sample from 1.0 to 1.5 h were observed. After 1.5 h, the recycling efficiencies of Cd dropped, but all curves seem to present an asymptotic behavior. The recycling efficiencies of Cd showed fluctuations during each of the temperature intervals. From 973 to 1073 K, the recycling efficiencies of Cd improved dramatically. However, the recycling efficiencies of Cd at 1073 K and 1173 K were almost the same. Tests at 973 K were less efficient than at 1073 K and 1173 K. Tests at 973 K, the maximum recycling efficiency of Cd was 92.58%. The curves at 1073 K and 1173 K tend to 100% in 2.5 h. The recycling efficiencies of Cd at 1073 K and 1173 K were calculated as 99.98%

and 99.99%, respectively, after 2.5 h of reduction. Tests at 1073 K and 1173 K presented a recycling efficiency of Cd of 99.99% after 3 h, respectively.

3.2.1.3. Effects of the loaded height and the addition of carbon powder on the recycling of Cd. Fig. 3 indicates that the effects of the loaded height and the addition of carbon powder on the recycling of Cd are minor. This may be attributed to the fact that the Cd attached to the steel belt with large porosity and the load of raw materials in each vacuum test were loose. Cadmium vapor can easily pass through the Fe and Ni particles and pass into the chamber and then is condensed in the condensation room. Therefore, the influence of the loaded height on the recycling of Cd is slight.

According to a report by Espinosa and Tenorio (2004), the organic material existing in waste Ni–Cd batteries, can acts as a reduction agent. The addition of carbon powder has no significant effect on the recycling of Cd due to the fact that some components of waste Ni–Cd batteries, which were not separated during the dismantling and crush processing and remain attached to the electrode, may be employed as reducing agent in the vacuum metallurgy separation process. This result is consistent with Espinosa and Tenorio's studies (Espinosa and Tenorio, 2004). Fig. 3 indicates

that 2 wt.% reducing agent in the reactions in this system was sufficient. This result is also consistent with the stoichiometric relation. This is attributed to the fact that although the valence and state of cadmium in the negative electrode are dependent on the state of charge and metal cadmium, $\text{Cd}(\text{OH})_2$ and CdO can be in existence in the electrode, 2 wt.% amounts of carbon powder was sufficient even the state of cadmium were all $\text{Cd}(\text{OH})_2$ according to the stoichiometric relation.

3.2.1.4. Analysis of range and variance. According to the calculation, the ranges of A, B, C, and D are 12.9, 7.8, 1.8, and 1.6, respectively, which indicate the sequence of four factors influencing the recycling of Cd are temperature, heating time, the addition of carbon powder, and the loaded height, respectively. In order to examine the significance of the selected factors on the recycling of Cd, variance analysis was conducted as shown in Table 4. In statistics, p -value is to evaluate the significance of process. When p -value is less than 0.05, the whole statistical process is significant (Qin et al., 2009). According to Table 4, it is noted that the temperature and heating time have a highly statistical significant in V_1 tests, with the p -values much less than 0.05. Whereas the loaded height and the addition of carbon powder are not significant since the p -value is more than 0.05. However, the addition of carbon powder cannot be eliminated from the model. This is attributed to the fact that the Cd can be removed completely from waste Ni–Cd batteries only if the sufficient carbon powder is added.

3.2.2. The optimum operating parameters of vacuum metallurgy separation processing

The optimum condition inducing the maximum recycling efficiency of Cd through range analysis was $A_4B_4C_4D_1$ (consist of $A = 1073 \text{ K}$, $B = 2.5 \text{ h}$, $C = 2 \text{ wt.}\%$, and $D = 30 \text{ mm}$, respectively). According to the results of V_2 tests, the recycling efficiency of Cd under the condition of $A_4B_4C_4D_1$ reached up to 99.98%.

The recycling efficiency of Cd can be improved by increasing the temperature or heating time. However, the temperature exceeding 1073 K not only highly depends on equipment investments, but also induces the distillation of other high vapor pressure metals such as zinc, which can be condensed with Cd and decreases its purity (Huang et al., 2009b). Furthermore, in view of the fact that the tests at 1073 K approached a 100% recycling, and the higher temperature or heating time will increase the energy consumption. To minimize the mass of the Cd with lower energy consumption, the optimum parameters can be set up as temperature = 1073 K, heating time = 2.5 h, the loaded height = 30 mm, and the addition of carbon powder = 2 wt.%.

According to a report by Xu, fractional condensation can avoid zinc condense with Cd (Huang et al., 2009b). Therefore, the fractional condensation was adopted in this study. Under the optimized condition, the good recycling results were obtained and the condensed Cd was collected. According to the XRD and ICP-AES analyzed results, the condensed product was characterized as metallic Cd as shown in Fig. 6, and the purity

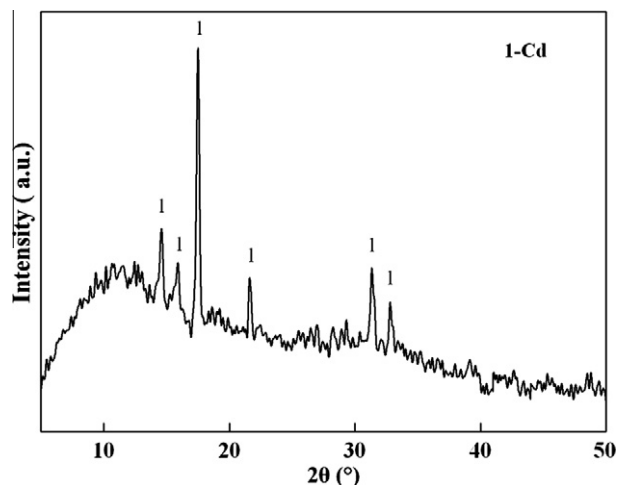


Fig. 6. X-ray diffraction pattern of condensed materials. Radiation: $\text{Cu}(\text{K}\alpha)$.

of Cd was 99.99%. Metallic Ni was detected as the main phase of the materials remaining in the crucible. A Ni–Co alloy containing less than 0.01 wt.% Cd was obtained as products of the recycling. The mass of the alloy can be negligible. Therefore, cadmium from waste Ni–Cd batteries was effectively recycled. The negative impacts on ecology quality and human health resulting from Cd can be resolved effectively through vacuum metallurgy separation.

4. Conclusions

It has been shown in the present study that,

1. High liberation efficiencies of the electrode materials could be attained in a crushing processing.
2. The characterization and the vacuum tests performed with waste Ni–Cd batteries show that it is able to effectively recycle cadmium from waste Ni–Cd batteries of different brands and models by using vacuum metallurgy separation. The temperature has most significant effect on the recycling of Cd, followed by heating time, and there are no much differences for the recycling efficiency of Cd by different the addition of carbon powder and the loaded height in the vacuum separation processing. The recycling efficiency of Cd was highest, with lower energy consumption, in the condition of temperature = 1073 K, heating time = 2.5 h, the loaded height = 30 mm, and the addition of carbon powder = 2 wt.%, respectively.
3. The residues fractions after vacuum separation processing should be evaluated in separate to be appropriately disposed of and the related experiments will be carried out in the future.
4. It was found that the orthogonal design of experiment is an effective tool for investigating a multifactor process, as well as for the vacuum metallurgy separation for waste Ni–Cd batteries. Application of orthogonal design in vacuum metallurgy separation process can effectively optimized the operating parameters. Therefore, this research enriches the vacuum metallurgy separation theory, and provides a theoretic basis for the optimization of operating parameters. It is feasible for recycling waste Ni–Cd batteries in scale-up.
5. Based on the experimental results, it is thus concluded that as well as waste Ni–Cd batteries, the other solid wastes, which contain the metals with high vapor pressure and low boiling point, can be effectively recycled by using the orthogonal design and vacuum metallurgy separation, to attain both environmental and economic benefits.

Table 4

Variance analysis for the V_1 tests.

Source	DF ^a	SS ^b	MS ^c	F-value	P-value
A	3	461.53	153.81	26.13	0.00001
B	3	164.71	54.94	9.34	0.005
C	3	8.74	2.91	0.49	0.597
D	3	6.01	2.02	0.34	0.323
E ^d	3	17.82	5.90		
Total	15	658.71			

^a Degree of freedom.

^b Sums of squares.

^c Mean square.

^d Error.

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